16

INFRARED SPECTRA OF *O*-BROMOPHENOL IN THE LIQUID STATE AND IN SOLUTIONS IN DIFFERENT SOLVENTS*

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ABSTRACT. The infrared spectra of *o*-bromophenol in the liquid state and in solutions in carbon tetrachloride, cyclohexane and chloroform in the 3200-3700 cm^{-1} region have been studied with a Perkin-Elmer Model 21 spectrophotometer. As regards the OH band, the pure liquid exhibits a broad absorption band at about 3460 cm^{-1} while sharp peaks at 3522, 3522 and 3490 cm^{-1} are exhibited by 3% solutions of the compound in carbon tetrachloride, cyclohexane and chloroform respectively. In the case of 12% solutions in carbon tetrachloride and cyclohexane, sharp peaks at 3474 and 3484 cm^{-1} are observed. In each of these two cases there is also an inflexion at about 3540 cm^{-1}.

It has been concluded that in the liquid state most of the molecules are present as dimers as suggested by Pauling and in the case of the dilute solutions the majority of the molecules are single. It has been pointed out that an idea of relative abundance of associated molecules and single molecules can be found from a comparison of the areas of the absorption peaks due to these two types of molecules present in concentrated solutions.

INTRODUCTION

In explaining the infrared spectrum of *o*-chlorophenol, Pauling (1945) pointed out that the liquid may contain double molecules formed through O-H...O intermolecular bond, while the OH group and chlorine atom of the same molecule may be linked in the *cis*-position. In a recent investigation on the infrared spectra of dilute solutions of *o*-chlorophenol in carbon tetrachloride and cyclohexane (Sirkar *et al.*, 1958) it was observed that the intermolecular hydrogen bond in associated molecules breaks up in dilute solutions. Davies (1940) studied the infrared spectrum of *o*-bromophenol in dilute solutions in carbon tetrachloride and observed a band at 3520 cm^{-1} and a weaker one at 3595 cm^{-1}, which were assigned by him to the O–H frequencies in the case of the OH group respectively in *cis*- and *trans*-position with respect to the bromine atom in the same molecule. Similar investigations in the first harmonic region were also reported by Wulf *et al.* (1936). They, however, did not report any data for the pure liquid. In the

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present work it was, therefore, intended to study the nature of hydrogen bonding in *o*-bromophenol in the liquid state and the influence of environment on the population of such associated molecules, and the infrared spectra of *o*-bromophenol in the liquid state and in solutions of different concentrations in carbon tetrachloride, cyclohexane and chloroform, have been studied. The results have been discussed in the present paper.

EXPERIMENTAL

Chemically pure *o*-bromophenol purchased from E. Merck was fractionated and the proper fraction was collected and redistilled under reduced pressure. Carbon tetrachloride, cyclohexane and chloroform used as solvents were also of chemically pure quality and were also distilled under reduced pressure before use.

The infrared spectra were recorded with a double beam Perkin-Elmer Model 21 spectrophotometer with rocksalt optics. The slit was adjusted at 927. The instrument was placed in an airconditioned room maintained at a temperature of 26°C.

The strengths of solutions used were 3% and 12% for solution in carbon tetrachloride and cyclohexane and 3% for solution in chloroform. The thickness of the cell was 0.1 mm in the case of dilute solutions and 0.025 mm in the case of the concentrated solutions. The spectrum of the pure liquid was recorded using a thin film of the liquid pressed between two rocksalt plates. In studying the spectra of the solutions, the bands of the solvents were eliminated by using an equivalent compensation cell containing the solvents in the reference beam.

RESULTS AND DISCUSSION

The absorption curves due to *o*-bromophenol and its solutions in carbon tetrachloride, cyclohexane and chloroform are reproduced in Figs. 1 and 2. In the case of the pure liquid broad absorption extending from 3550 cm^{-1} to 3200 cm^{-1} is observed which suggests that the absorption curve is produced by superposition of more than one broad bands. The maximum of absorption is at about 3460 cm^{-1} which is broadened towards lower frequencies with a gradual fall in intensity. In 3% solution in carbon tetrachloride and cyclohexane, however, the intense broad band at 3460 cm^{-1} is totally absent and only a sharp peak at 3522 cm^{-1} is observed. Davies (1940) observed a band at 3520 cm^{-1} and a very much weaker band at 3595 cm^{-1} in the spectrum of .09M solution of *o*-bromophenol in carbon tetrachloride. He attributed the first band to the O–H vibration in the OH group in the *cis*-position with respect to bromine atom and the second one to the O–H group in the *trans*-position. On comparing these results, it appears that the intense broad peak at 3460 cm^{-1} in the pure liquid may represent the O–H vibration in the dimeric molecules present in the liquid, the

hydrogen atom of the OH group of a molecule being attached to the oxygen atom in a neighbouring molecule (Pauling, 1945).

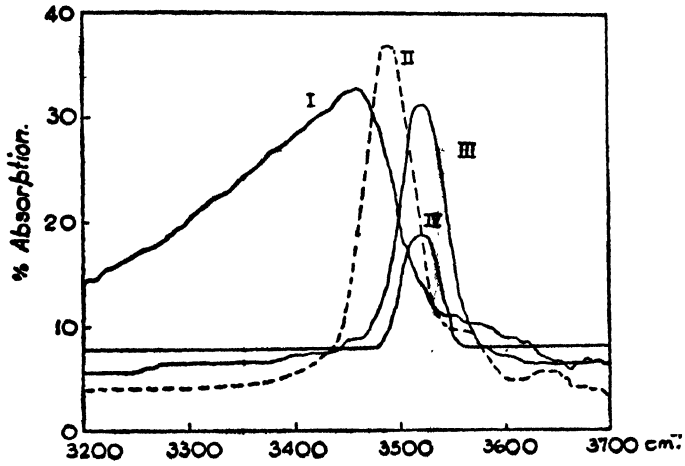

Fig. 1. Infrared absorption spectra of o-bromophenol
Curve I. Pure liquid
Curve II. 3% solution in chloroform
Curve III. 3% solution in carbon tetrachloride
Curve IV. 3% " " cyclohexane

When the molecules are dispersed in 3% solutions in carbon tetrachloride and cyclohexane, the intermolecular O–H...O bond is broken and the observed frequency at 3522 cm^{-1} represents the O–H stretching oscillation in the OH group in the single molecule. As pointed out in a previous paper (Sirkar *et al.*, 1958) this frequency may not belong to *cis*-configuration. The peak due to solution in CCl_4 is, however, much larger than that due to the solution in cyclohexane. This shows the influence of the environment on the strength of absorption . The weak OH stretching band assigned to *trans*-molecules reported by Davies has, however, not been observed in the present investigation. In 3% solution of *o*-bromophenol in the polar solvent chloroform, the OH vibrational frequency is only at 3490 cm^{-1}, which may indicate an influence of the field of the polar solvent molecules on this frequency of the dispersed molecules of *o*-bromophenol.

When the concentration of *o*-bromophenol in carbon tetrachloride and cyclohexane is increased to 12%, sharp peaks at 3474 and 3484 cm^{-1} respectively are observed. In this case the strength of absorption is also relatively higher than at 3522 cm^{-1} in the case of the 3% solution with equivalent path length. This peak is accompanied in each case by a weak inflexion at about 3540 cm^{-1}. Thus the concentrated solutions in both the solvents seem to contain large number of dimeric molecules and a few single molecules and the two frequencies due to

each of these 12% solutions probably represent OH stretching oscillations in intermolecular OH...O bonded group and in the OH group in the *trans*-position in the single molecule as pointed out by Sirkar *et al.* (1958).

It is interesting to note that the results discussed above give definite indication of the predominance of dimeric molecules in the pure liquid state of

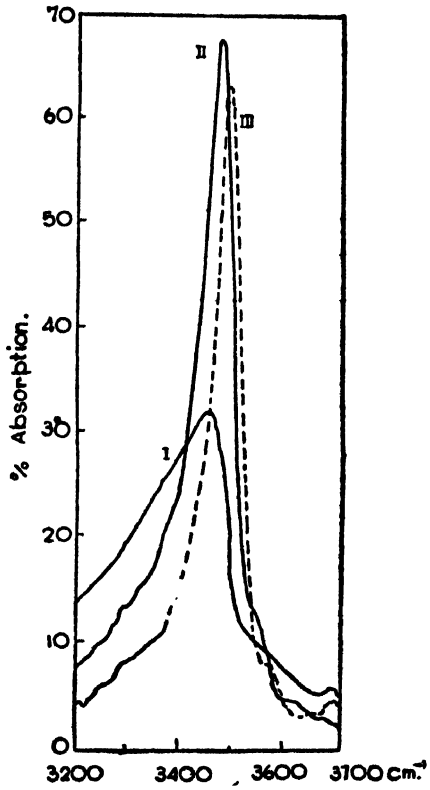

Fig. 2. Infrared absorption spectra of *o*-bromophenol
Curve I. Pure liquid
Curve II. 12% solution in carbon tetrachloride
Curve III. 12% solution in cyclohexane

o-bromphenol and also give an idea about the relative abundance of dimeric molecules over the *trans*-type single molecules in the case of solutions of concentration above 10%. In fact, a quantitative estimation of the relative population of O–H...O bonded double molecules with OH group in *cis*-configuration with respect to that of the single molecules can be made from the ratio of the areas of the peaks at 3474 cm^{-1} and 3540 cm^{-1} respectively observed in the case of concentrated solutions if the change in the strength of absorption per molecule with the change from the *trans* to the *cis* position of the OH group is first determined.

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REFERENCES

Davies, M. M., 1940, *Trans. Faraday. Soc.*, **36**, 333.
Pauling, L., 1945, The Nature of the Chemical Bond, p. 324.
Sirkar, S.C., Deb, A. R. and Banerjee, S.B., 1958, *Ind. J. Phys.*, **32**, 345.
Wulf, O.R., Liddel, U. and Hendricks, S. B., 1936, *J. Am. Chem. Soc.*, **58**, 2287.,